

# An efficient Multiple Scattering method based on partitioning of scattering matrix by angular momentum and approximations of matrix elements

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**Abstract.** We present a numerically efficient and accurate Multiple Scattering formalism, which is a generalization of the Multiple Scattering method with a truncated basis set [X. -G. Zhang and W. H. Butler, Phys. Rev. B 46,7433 (1992)]. Compared to the latter method, we keep the phase shifts of high angular momenta but apply approximations in the matrix elements of the scattering matrix  $(I - tg)$ , which is the subtraction of the unit matrix and the product of transition operator matrix and structure constant matrix. We have discussed the detailed behaviour of our formalism for some different types of calculations, where not full information of Green's function is needed. We apply our formalism to study density of states of fcc Cu and silicon and C K-edge X-ray absorption spectra of graphene, in order to check the efficiency and accuracy of our formalism. It is found that compared to Zhang's method, the accuracy is greatly improved by our method.

## 1. Introduction

Multiple Scattering (MS) theory was proposed originally by Korringa and by Kohn and Rostoker (KKR) as a convenient method for calculating the electronic structure of solids [1, 2] and was later extended to polyatomic molecules by Slater and Johnson [3]. It has been widely applied to the computation of the electronic structure [4, 5, 6] and spectroscopies [7, 8, 9] of various systems, such as crystals, molecules, surfaces, alloys, as well as systems with defects and adsorbates.

In MS, wavefunctions are expanded in a spherical-wave basis, which is the local numerical solution of the Schrodinger equation (SE). In practice, the size of basis sets is truncated to a particular orbital angular momentum -  $l_{max}$ . For some studies where accuracy is not very crucial or angular moment convergence is very fast,  $l_{max}$  can be reasonably chosen to a small value, e.g., 2, 3 or 4. However, in some applications or if we need higher accuracy,  $l_{max}$  will be not that small, e.g., 6 to 8 or even higher. The MS computation for one energy point consists of three steps: (i) Solving the single-site SE to obtain the transition operator matrix  $t_{LL'}^i$ , and constructing the structure constant matrix  $g_{LL'}^{ij}$ , where  $i$  represents a scattering site and  $L \equiv (l, m)$  is the combination of orbital and magnetic angular momenta. The definition of  $t_{LL'}^i$  is given in Eq. 5 of Sec. 2.1. (ii) Inverting the scattering matrix which is defined in our formalism as  $I - tg$ , where  $I$  represents the unit matrix. (iii) Computing the Green's function and the studied properties.

Nowadays, when deal with nanostructured systems, molecular adsorption on surface, systems with impurities and some complicated materials, e.g., lithium ion battery, people have to build huge unitcells or cluster models for computations. Therefore, it becomes important to reduce the computation time without much loss of accuracy. In MS calculations, since the computation time of matrix inversion is proportional to the cube of the dimension of the matrix, if the system is large, as in addition we usually need tens of or more energy points, the whole process will be very time-consuming. In MS theory, we have observed a fact that the contribution of high angular momenta is much smaller than that of low angular momenta and can be considered as a perturbation. Therefore, we expect the contribution of these high angular momenta to be included efficiently in some approximative ways without loss of accuracy.

Zhang *et al.* [10] suggested an approximate method where the phase shifts of high angular momenta ( $l_{pt} < l \leq l_{max}$ ) are neglected, so that the computation is considerably simplified. They obtained a good normalization of the wavefunction with small  $l_{pt}$ . Applications and more discussions are given by R. Zeller [11] and A. Alam *et al.* [12].

However, it was found that when Muffin-Tin (MT) approximation does not work or when angular momentum convergence is slow, Zhang's method may not be so accurate, so that it becomes necessary to go beyond. In our formalism, while keeping to solve single-site problem with  $l_{max}$ , we introduce approximations directly to the elements of

the scattering matrix  $I - tg$ : some unimportant elements are neglected, so that some submatrices of  $I - tg$  become sparse. While our formalism loses no or a little efficiency, the accuracy is improved considerably compared to Zhang's method.

## 2. Formalism

### 2.1. Two forms of Green's function

Our formalism is based on the Full-Potential Multiple Scattering (FPMS) theory with space-filling cells developed by K. Hatada *et al.* [13, 14, 15]. Here, space is partitioned by nonoverlapping space-filling cells or Voronoi polyhedra. When a Voronoi polyhedron does not contain any atom or is in the interstitial region but still contains charge density, it is called an empty cell (EC). The local Schrödinger equation is solved without the limit of the geometrical shape of the potential, since the potential is not expanded in spherical harmonics.

In MS theory, two forms of Green's function are commonly used:

$$G(\vec{r}_i, \vec{r}_j; E) = \sum_{LL'} \bar{\Phi}_L^i(\vec{r}_i) ([I - tg]^{-1} t)_{LL'}^{ij} \bar{\Phi}_{L'}^j(\vec{r}_j) - \delta_{ij} \sum_L \bar{\Phi}_L^i(r_{<}^i) \Lambda_L^i(r_{>}^i) \quad (1)$$

and

$$G(\vec{r}_i, \vec{r}_j; E) = \sum_{LL'} \underline{\Phi}_L^i(\vec{r}_i) (g[I - tg]^{-1})_{LL'}^{ij} \underline{\Phi}_{L'}^j(\vec{r}_j) - \delta_{ij} \sum_L \underline{\Phi}_L^i(r_{<}^i) \Psi_L^i(r_{>}^i) \quad (2)$$

where  $\vec{r}_i$  is the coordinate with respect to the center of scattering site  $i$ .  $\Psi$  and  $\Lambda$  are the irregular solutions of local Schrödinger equation which match smoothly to spherical Hankel and Bessel functions, respectively, at the cell boundary.  $r_{<}(r_{>})$  is the smaller (larger) of  $r$  and  $r'$ . The definitions of  $\underline{\Phi}$  and  $\bar{\Phi}$  are:

$$\bar{\Phi}_L \equiv \sum_{L'} S_{L'L}^{-1} \Phi_{L'} \quad (3)$$

and

$$\underline{\Phi}_L \equiv \sum_{L'} E_{L'L}^{-1} \Phi_{L'}, \quad (4)$$

where  $\Phi$  is the solution of local Schrödinger equation which behaves as the spherical Bessel function of the first kind at the origin. The definitions of  $E$  and  $S$  matrices will be given in Appendix and they are computed using values on the surface of the bounding sphere of the cell.

The transition operators are defined as

$$t_{LL'} = - \sum_{L''} S_{LL''} (E^{-1})_{L''L'}. \quad (5)$$

The first form of Green's function in Eq. 1 is more efficient than the second form in Eq. 2, since multiplying matrix  $[I - tg]^{-1}$  by site-diagonal matrix  $t$  is much easier than multiplying  $[I - tg]^{-1}$  by  $g$ . Actually, in MS theory, usually  $[I - tg]^{-1} t$  is defined as matrix  $\tau$ . On the other hand, the second form of Green's function in Eq. 2 is numerically a bit more stable, since  $S$  matrix and  $\Lambda$  functions have poles on the real energy axis. Through the end of this article, we will only apply the first form.

## 2.2. Matrix partitioning and approximations for matrix inversion

We define matrices  $M = I - tg$  and  $\mathcal{M} = [I - tg]^{-1}$ . These matrices are truncated at  $l_{max}$ . If we partition  $M$  by a particular orbital angular momentum  $l_{pt}$  into four submatrices, we have

$$M = \begin{bmatrix} M_{ss'} & M_{sb'} \\ M_{bs'} & M_{bb'} \end{bmatrix} = \begin{bmatrix} A & B \\ C & D \end{bmatrix}, \quad (6)$$

where the subscript  $s$  ( $s'$ ) and  $b$  ( $b'$ ) correspond respectively to  $l$  small ( $0 < l \leq l_{pt}$ ) and large ( $l_{pt} < l < l_{max}$ ). The submatrices are:

$$A = I - t_{sf}g_{fs'}, \quad (7)$$

$$B = -t_{sf}g_{fb'}, \quad (8)$$

$$C = -t_{bf}g_{fs'}, \quad (9)$$

$$D = I - t_{bf}g_{fb'}, \quad (10)$$

where the subscript  $f$  indicates that the full angular momenta are included. The Einstein summation convention is used, and the summations are only on two neighboring subscripts.

We define also

$$\mathcal{M} = \begin{bmatrix} \mathcal{M}_{ss'} & \mathcal{M}_{sb'} \\ \mathcal{M}_{bs'} & \mathcal{M}_{bb'} \end{bmatrix} = \begin{bmatrix} \mathcal{A} & \mathcal{B} \\ \mathcal{C} & \mathcal{D} \end{bmatrix}. \quad (11)$$

Therefore, we have the relations:

$$\mathcal{A} = [A - BD^{-1}C]^{-1}, \quad (12)$$

$$\mathcal{B} = -\mathcal{A}BD^{-1}, \quad (13)$$

$$\mathcal{C} = -D^{-1}C\mathcal{A}, \quad (14)$$

$$\mathcal{D} = D^{-1} + D^{-1}C\mathcal{A}BD^{-1}. \quad (15)$$

Usually matrix  $A$  is very dense. Except for the diagonal elements, the elements of matrix  $D$  are very small, so that we approximate  $D$  and  $D^{-1}$  by the unit matrix. This approximation works well when we study the energy region below or several tens of electron volt (eV) above the Fermi level. Afterwards, we have the approximate relations:

$$\mathcal{A} = [A - BC]^{-1}, \quad (16)$$

$$\mathcal{B} = -\mathcal{A}B, \quad (17)$$

$$\mathcal{C} = -C\mathcal{A}, \quad (18)$$

$$\mathcal{D} = I + C\mathcal{A}B. \quad (19)$$

In this work, matrix  $D$  is always approximated by the unit matrix, i.e., we will use Eq. 16 - 19 instead of Eq. 12 - 15.

A further approximation is to treat  $B$  as a sparse matrix. In Sec. 3, we prove that this approximation works well. The way to construct an approximate matrix of  $B$  is straightforward: a particular percentage, e.g., 1%, of elements, whose absolute values

are larger than the rest are kept in matrix  $B$  while all the others are set to zero. The computation time of sparsification is then proportional to the size of the matrix  $B$ . Furthermore, the fact, that the threshold absolute value used to make matrix  $B$  sparse varies slowly with energy, makes this computation even cheaper. Whether  $C$  can be approximated by a sparse matrix for computing  $\mathcal{C}$  and  $\mathcal{D}$  needs further studies, but we have checked that it is not satisfactory to treat  $C$  as a sparse matrix for computing  $\mathcal{A}$ .

### 2.3. Comparisons with Zhang's method

The original Zhang's method uses the second form of Green's function (Eq. 2) and neglects the phase shifts of high angular momenta. It can be seen as the combination of two approximations: (i) The spherical-wave basis is truncated by  $l_{pt}$ , so that when  $l_{pt} < l \leq l_{max}$ ,  $\Phi_L$  and  $\Psi_L$  are respectively the spherical Bessel and Hankel functions. (ii) For matrix  $I - tg$ ,  $t_{LL'}$  with  $l > l_{pt}$  or  $l' > l_{pt}$  is approximated by zero, so that,  $B = -t_{ss'}g_{s'b}$  (Eq. 9) and  $C = 0$  (Eq. 8).

Zhang's method works well when MT approximation is valid and angular momentum convergence is fast. However, it may be not suitable when MT approximation behaves poorly or breaks down because of the following three points:

(i)  $\Phi_L = \sum_{L'} R_{L'L} Y_{L'}$  and  $\Phi_L$  with  $l < l_{pt}$  is now strongly affected when increasing  $l_{pt}$ , while in MT approximation,  $\Phi_L = R_l Y_L$  with  $l < l_{pt}$  is not affected by the chosen of  $l_{pt}$ .

(ii) The absolute value of  $t_{LL'}$  with  $l$  or  $l' > l_{pt}$  may not be small now. On the other hand, in MT approximation,  $t_{LL'} = \delta_{LL'} t_l$  so that the off-diagonal terms are zero, and  $t_l$  with  $l > l_{pt}$  is usually quite small if  $l_{pt}$  is not small. This point may strongly break the second approximation of Zhang's method. In the application of X-ray absorption spectroscopy (XAS) of graphene, we have observed that the absolute value of  $t_{LL'}$  with  $l > l_{pt}$  and  $l' \leq l_{pt}$  can be quite large.

(iii) The angular momentum convergence may be slower now, if the potential is highly anisotropic. By contrast, in MT approximation, this convergence is mainly controlled by the energy, so that when we study the low energy region, a standard calculation with  $l_{max}=2$  or 3 can already give reasonable results for some physical properties.

It should be noticed that in the following discussions, when we mention Zhang's method, it always contains only the second approximation.

### 2.4. Formalism in different types of calculations

In many studies, the full information contained in Green's function is not necessary, that is to say, only parts of elements of matrix  $\tau$  defined in Sec. 2.1 are needed. For the following discussion, we define the number of scattering sites as  $N_{sc}$ , and the dimension of matrix  $A$  and  $D$  as  $a = N_{sc}(l_{pt} + 1)^2$  and  $b = N_{sc}[(l_{max} + 1)^2 - (l_{pt} + 1)^2]$  respectively. Moreover, in this work, matrix  $D$  is always approximated by the unit matrix, i.e., Eq.

16 - 19 are applied. There are many methods to compute the full or partial matrix inversion, In this work, we only use LU decomposition.

**2.4.1.  $\tau^{00}$  or  $\tau^{i0}$**  Here, "0" represents one particular scattering site while "i" can be any site. For core-level spectroscopies, only  $\tau^{00}$  is needed and "0" is restricted to the absorber where a core electron is excited. For photoemission, what we need is  $\tau^{i0}$ .

$\tau^{i0}$  can be computed in the following steps:

1. Compute  $BC$ . The number of multiplications  $N_{op}$  is  $c_s p a^2 b$ , where  $p$  is the percentage of nonzero elements of  $B$ . As  $l_{pt}$  and  $N_{sc}$  increase, we can expect that  $p$  can be suitably chosen as a smaller value.  $c_s$  ( $>1$ ) is introduced to consider the fact that the implementation of matrix multiplication of a sparse matrix by a dense matrix is often not well performed so that the efficiency is less than expected, or needs additional operations other than the necessary multiplications and summations of two values, although  $c_s$  does not really affect the number of multiplications. In this work, the normal dense matrix multiplication is done using the LAPACK math library, while a sparse matrix being multiplied by a dense matrix is done without the use of any math library. Therefore,  $c_s$ , in this work, is about 3.

2. Compute  $\mathcal{A}^{j0}$ . By LU decomposition, we obtain  $A - BC = LU$ , where  $L$  and  $U$  are respectively a lower and a upper triangular matrix. The computation is dominated by LU decomposition, so that  $N_{op} \approx a^3/3$ .

3. Compute  $\mathcal{B}^{j0}$ . We just need to solve  $(l_{max} + 1)^2 - (l_{pt} + 1)^2$  linear equations, so that the complexity of this process is  $O(a^2)$ .

4. Compute  $\mathcal{C}^{j0}$ . The complexity of this process is  $O(ab)$ .

5. Compute  $\mathcal{D}^{j0}$ . The complexity of this process is  $O(ab)$ .

6. Compute  $\tau^{i0} = \mathcal{M}^{i0} t^0$ . The complexity of this process is  $O(a + b)$ .

The whole computation is dominated by the first two steps, so that  $N_{op} \approx a^3/3 + c_s p a^2 b$ , if  $N_{sc}$  is not small. For the computation of  $\tau^{00}$ ,  $N_{op}$  is smaller but still approximated by  $a^3/3 + c_s p a^2 b$ , if  $N_{sc}$  is not small. In Zhang's method, since  $C = 0$ ,  $N_{op} \approx a^3/3$ . In standard calculations, the computation time is dominated by the LU decomposition of the full  $M$  matrix, so that  $N_{op} = (a + b)^3/3$ . If  $l_{max} = 6$ ,  $l_{pt} = 3$ ,  $p = 1\%$  and  $c_s = 3$ ,  $N_{op}$  of our method is about 4.1% of  $N_{op}$  of the standard calculation.

**2.4.2.  $\tau^{ii}$**  For the calculations of the density of states (DOS) and related quantities, e.g., the total energy, only the site-diagonal elements of matrix  $\tau$ , i.e.,  $\tau^{ii}$ , are needed.  $\tau^{ii}$  can be computed in the following steps:

1. Compute  $BC$ .  $N_{op} = c_s p a^2 b$ .

2. Compute  $\mathcal{A}^{ii}$ .  $N_{op} = a^3$ .

3. Compute  $\mathcal{B}^{ii}$ . the complexity of this process is  $O(N_{sc}^2)$ .

4. Compute  $\mathcal{C}^{ii}$ . From Eq. 18, the complexity of this process is  $O(N_{sc}^2)$ .

5. Compute  $\mathcal{D}^{ii}$ . From Eq. 17 and 19, the complexity of this step is  $O(N_{sc}^2)$ .

6. Compute  $\tau^{ii} = \mathcal{M}^{ii} t^i$ . The complexity is  $O(N_{sc})$ .

The total number of multiplications is  $N_{op} \approx a^3 + c_s p a^2 b$ , while in standard calculations,  $N_{op} = (a + b)^3$ . In Zhang's method,  $N_{op} \approx a^3 + a^2 b$ . If  $l_{max} = 6$ ,  $l_{pt} = 3$ ,  $p = 1\%$  and  $c_s = 3$ ,  $N_{op}$  in our method is about 3.7% of  $N_{op}$  of the standard calculation.

*2.4.3. Density of states* The total DOS is

$$n(E) = \sum_i n_i(E) + n_I(E), \quad (20)$$

where  $n_I(E)$  is the DOS of the interstitial charge. If space is filled by Voronoi polyhedra,  $n_I(E)$  will reduce to zero.  $n_i(E)$  is the integral DOS in the cell  $i$ ,

$$n_i(E) = -\frac{1}{\pi} \text{Im} \int_{\Omega_i} G(\vec{r}, \vec{r}, E) d\vec{r}. \quad (21)$$

We substitute  $\Phi_L(\vec{r}) = \sum_{L'} R_{L'L}(r) Y_{L'}(\hat{\vec{r}})$ ,  $\Lambda_L(\vec{r}) = \sum_{L'} \bar{R}_{L'L}(r) Y_{L'}(\hat{\vec{r}})$ , where  $Y_L$  are the real spherical harmonics, Eq. 3 and Eq. 1 into the above equation. We obtain

$$n_i(E) = -\frac{1}{\pi} \text{Im} \left[ \sum_{LL'} \left( \tau_{LL'}^{ii} \sum_{L_1 L_2} S_{L_1 L}^{-1} S_{L_2 L'}^{-1} \rho_{L_1 L_2} \right) + \sum_{L'L} S_{L'L}^{-1} \bar{\rho}_{L'L} \right], \quad (22)$$

$$\rho_{L_1 L_2} = \sum_{L_3 L_4} \int r^2 dr R_{L_3 L_1}(r) R_{L_4 L_2}(r) \int d\hat{\vec{r}} Y_{L_3}(\hat{\vec{r}}) Y_{L_4}(\hat{\vec{r}}) \theta(\vec{r}), \quad (23)$$

$$\bar{\rho}_{L'L} = \sum_{L_3 L_4} \int r^2 dr \bar{R}_{L_3 L'}(r) R_{L_4 L}(r) \int d\hat{\vec{r}} Y_{L_3}(\hat{\vec{r}}) Y_{L_4}(\hat{\vec{r}}) \theta(\vec{r}), \quad (24)$$

where  $\theta(\vec{r})$  is the shape function which vanishes outside the cell. For the sake of simplicity, we only calculate in this work the local DOS  $n_i^{in}(E)$  where the integration region is limited to the inscribed sphere of a cell, so that

$$\int d\hat{\vec{r}} Y_{L_3}(\hat{\vec{r}}) Y_{L_4}(\hat{\vec{r}}) \theta(\vec{r}) = \delta_{L_3 L_4}, \quad (25)$$

and

$$\rho_{L_1 L_2} = \sum_{L_3} \int_0^{R^{in}} r^2 dr R_{L_3 L_1}(r) R_{L_3 L_2}(r), \quad (26)$$

$$\bar{\rho}_{L'L} = \sum_{L_3} \int_0^{R^{in}} r^2 dr \bar{R}_{L_3 L'}(r) R_{L_3 L}(r), \quad (27)$$

where  $R^{in}$  is the radius of the inscribed sphere. If  $r > R^{in}$ , we can use the relation

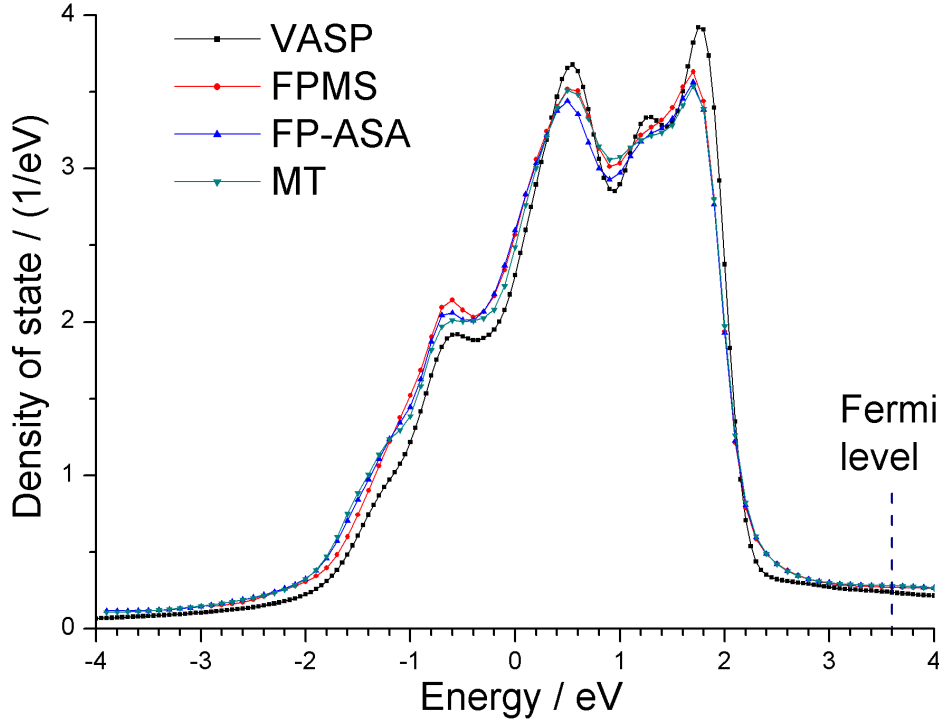
$$\int d\hat{\vec{r}} Y_{L_3}(\hat{\vec{r}}) Y_{L_4}(\hat{\vec{r}}) = \sum_{L_5} C(L_5 L_3 | L_4) Y_{L_5}(\hat{\vec{r}}), \quad (28)$$

where  $C(L_5 L_3 | L_4)$  is the Gaunt coefficient.

### 3. Results and discussions

#### 3.1. DOS of Cu crystal

For the standard test case, we first study a Cu crystal, for which it is well known that MT approximation is a good approximation. Therefore, we expect Zhang's method (see

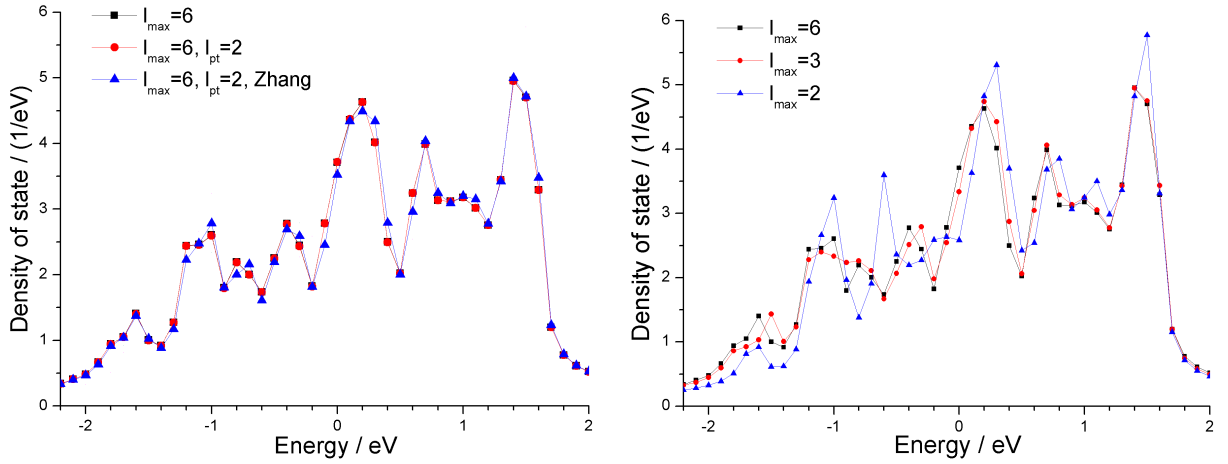


**Figure 1.** Calculated local DOS of a Cu sphere of radius 1.276 Å in fcc Cu crystal using different methods. VASP corresponds to the VASP code with PAW (Projector Augmented Wave) method. MT, FP-ASA and FPMS represent three kinds of Multiple Scattering calculations. "MT" uses Muffin-Tin approximation, while "FP-ASA" uses atomic-sphere approximation but inside each atomic sphere, potential is not approximated to spherical. In "FPMS", no approximation is applied to the shape of potential and space is partitioned by nonoverlapping space-filling cells or Voronoi polyhedra. For all MS calculations, a cluster of radius 11 Å, containing 459 atoms, is used.

Sec. 2.3) to work well. However, we will show that the accuracy is greatly improved by our method without any loss of efficiency (see the discussion of computation time in Sec. 2.4).

In Fig. 1, we compare the local DOS of a Cu sphere of radius 1.276 Å in fcc Cu crystal computed with different methods. To make the comparison easier, a 0.15 eV Gaussian broadening is used. VASP corresponds to the VASP code with PAW (Projector Augmented Wave) method. MT, FP-ASA and FPMS represent three kinds of Multiple Scattering calculations. "MT" uses Muffin-Tin approximation, while "FP-ASA" uses atomic-sphere approximation but inside each atomic sphere, potential is not approximated to spherical. In "FPMS", no approximation is applied to the shape of potential and space is partitioned by nonoverlapping space-filling cells or Voronoi polyhedra. In our FP-ASA and MT calculations, the diameters of the spheres are taken to be 10% larger than the nearest-neighbor distance. In the FPMS calculation, we have added an empty cell on the center of the fcc cube of the Cu crystal in order to fill the space.



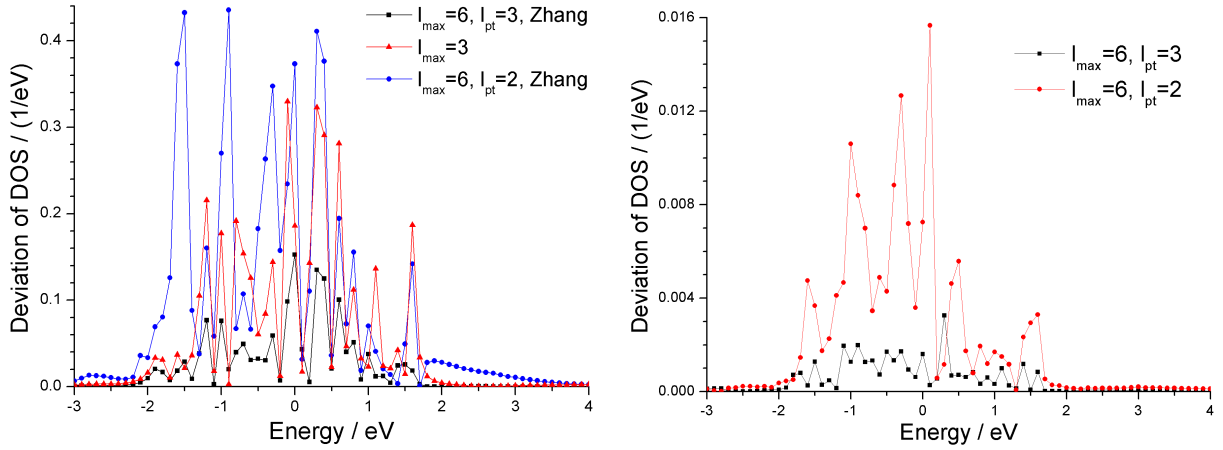


**Figure 2.** Calculated local DOS on the central Cu atom of a cluster, of radius 8 Å, containing 177 atoms, of fcc Cu crystal by the FPMS method. No additional Gaussian broadening is used.

In VASP calculation, the plane-wave cut-off energy is 400 eV and a  $9 \times 9 \times 9$  and  $21 \times 21 \times 21$  Monkhorst-Pack K-point sampling were used respectively to generate the charge density and compute the DOS. The exchange-correlation functional ( $V_{xc}$ ) proposed by Ceperley and Alder [18] and parameterized by Perdew and Zunder [19], named CA-PZ, has been employed.

In Fig. 1, in order to reproduce the bulk properties (so as to compare with VASP result) by our real-space MS calculations, in all three MS calculations, we use a huge cluster of radius 11 Å, containing 459 atoms. Moreover, for the optical potential, its real part is taken as CA-PZ  $V_{xc}$ , while its imaginary part is a small constant. By contrast, in Fig. 2 and 3, since our purpose is to check the new algorithm of matrix inversion, the radius of the cluster is chosen smaller as 8 Å, containing 177 atoms. Additionally, the real part of the optical potential is the Hedin-Lundqvist (HL) potential [20]. As we have checked, the MS results using CA-PZ  $V_{xc}$  and HL potential are different by mainly a small energy shift. The self-consistent charge density and electrostatic potential for MS calculation is obtained from the ES2MS package [21] from an all-electron charge density and a pseudo electrostatic potential generated by the VASP code. We treat  $l = 6$  as the converged value of  $l_{max}$ . However for simplicity, in Fig. 1,  $l_{max}$  is set to 5. We checked that the differences between the result using  $l_{max} = 5$  and that using  $l_{max} = 6$  is very small.

From Fig. 1, we see that all three MS results are similar to that by VASP code. The differences between MS and VASP results can be attributed to the following points: (i) A larger radius of the cluster may be needed for the better convergence of the MS calculation. (ii) The local DOS of Cu by VASP is the sum of s-, p- and d-electron DOS inside a sphere, since the VASP code usually does not give other components in the output files. (iii) MS uses an energy-dependent basis while the VASP calculation uses an energy-independent basis.



**Figure 3.** The absolute values of the deviations between the results of different FPMS calculations and the result of the standard FPMS calculation with  $l_{\max} = 6$ . The magnitude of the values in the right panel is much smaller than that in the left panel.

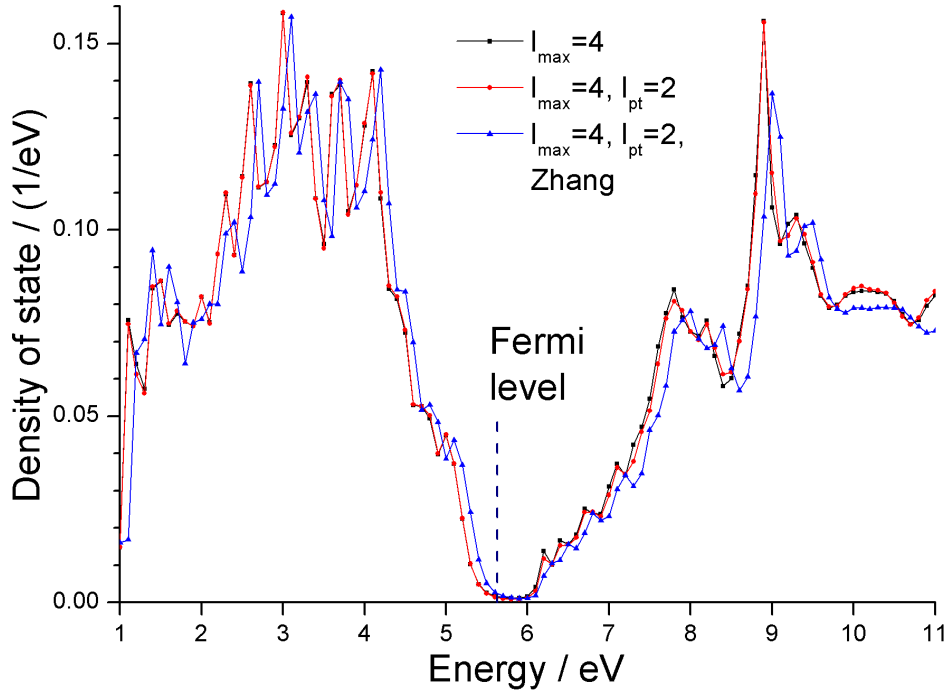
From Fig. 2, we can see the angular momentum convergence of the DOS of the Cu crystal is quite fast, e.g., the FPMS result with  $l_{\max} = 3$  is close to that with  $l_{\max} = 6$ . With  $l_{\max} = 6$  and  $l_{\text{pt}} = 2$ , the result by our method is nearly the same as the result of the standard calculation with  $l_{\max} = 6$ , while the result by Zhang’s method is worse but better than the  $l_{\max} = 3$  result.

Fig. 3 shows the absolute values of the deviations between results of different FPMS calculations and the result of the standard FPMS calculation with  $l_{\max} = 6$ . The accuracy of our method is tens of or one hundred times better than Zhang’s method.

### 3.2. DOS of silicon

As discussed in Sec. 2.3, when FP becomes important, the errors in Zhang’s method may be large. In open systems, especially when covalent bonds are present, MT approximation may fail. Moreover, from our experience, as the element studied becomes lighter, FP effects may be stronger. In Ref. [15], it was found that FP is necessary for  $\alpha$ -quartz. Therefore, in order to study silicon, FP is expected to be necessary. In Ref. [22], the authors have shown that FP effects are strong for graphene-related systems. In the following two subsections, we will study silicon and graphene systems where FP effects are large, and compare the results by Zhang’s and by our method.

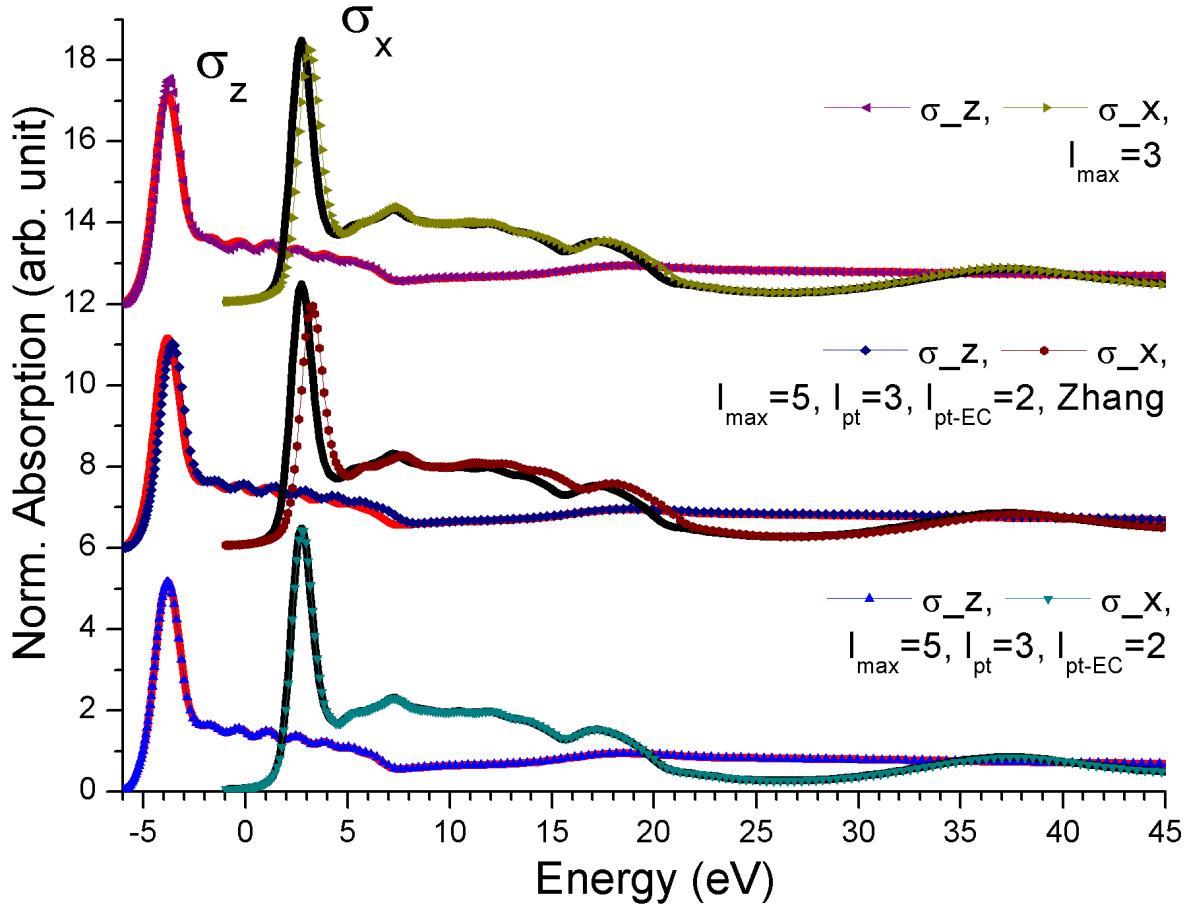
In order to reproduce the local DOS of the Si atom in silicon, a very large cluster may be needed for real-space methods [23]. For simplicity, we use a cluster of radius 24 Å, containing 2917 atoms. Moreover, we employ the  $T_d$  point group symmetry and focus only on the  $T_2$  irreducible representation so that we obtain the local projected DOS where the wavefunction is projected onto the basis  $(x, y, z)$ . Since the ground-state properties of silicon are dominated by  $p$ -electron orbitals, the local projected DOS obtained has a similar shape as the total DOS of silicon and can reproduce the same energy gap.



**Figure 4.** Calculated local projected DOS ( $T_2$  irreducible representation) of the central Si atomic sphere, of radius 1.175 Å, of a cluster of silicon by FPMS. The cluster radius is 24 Å, containing 2917 atoms. The energy gap calculated by our method, with  $l_{max} = 4$  and  $l_{pt} = 2$ , is very close to the gap calculated by VASP code, while the gap given by Zhang’s method is much worse. However, since LDA is applied to  $V_{xc}$  or optical potential, the energy gaps given by VASP calculation and our method are not very close to the experimental one.

We have checked that when we use a cluster of radius 18 Å, corresponding to 1207 Si atoms, the local DOS of the central Si atom obtained by FPMS is quite similar to the local DOS of the Si atom in silicon calculated with the VASP code, except that the DOS by FPMS at Fermi level is about 0.005 state per electron volt while it is much smaller when computed with the VASP code. Since we use the self-consistent crystal potential in our real-space cluster calculations, this potential is not suitable for scattering sites near the boundary of the cluster. While the DOS near the Fermi level is very sensitive to the accuracy of the potential, our real-space method is not suitable to study the ground-state properties of semiconductor crystals and nanocrystals. To solve this problem, the reciprocal-space version of our FPMS method and the self-consistent cluster potential are needed. Additionally, the truncated crystal approximation may be useful for constructing the cluster potential from a bulk calculation [24, 25].

In Fig. 4, we compare the local projected DOS ( $T_2$  irreducible representation) of the central Si atomic sphere, of radius 1.175 Å, of a cluster of silicon by the standard FPMS calculation with  $l_{max} = 4$ , by our approximate method with  $l_{max} = 4$  and  $l_{pt} = 2$  and by Zhang’s method with  $l_{max} = 4$  and  $l_{pt} = 2$ . Empty cells are added at the positions described in Ref. [26]. The errors on the result by our method is much smaller than those by Zhang’s method.



**Figure 5.** Calculated XAS of a graphene cluster of radius 20 Å, containing 481 Carbon atoms and 1902 empty cells. Three calculations are compared with the standard calculation with  $l_{max} = 5$ . The red (black) solid line represents  $\sigma_z(x)$  of XAS of graphene by the standard calculation with  $l_{max} = 5$ . " $l_{pt} = 3, l_{pt-EC} = 2$ " correspond respectively to  $l_{pt}$  of the atomic cells set to 3 and  $l_{pt}$  of the empty cells set to 2. "Zhang" corresponds to the Zhang's method (see Sec. 2.3).  $\sigma_{z(x)}$  is polarized absorption cross section with electric field along  $z(x)$  axis.

### 3.3. XAS of graphene

In Ref. [22], we have applied the real-space FPMS method with space-filling cells with self-consistent potential to study XAS of graphene and graphene oxide. The fact that good agreement with experiments was always achieved demonstrated the accuracy of our FPMS method. For simplicity, in this work, we focus on XAS of a graphene cluster of radius 20 Å, containing 481 Carbon atoms and 1902 empty cells. Computation details are given in Ref. [22].

In Fig. 5, we find that with our method, if we set  $l_{max} = 5$ ,  $l_{pt}$  of atomic and empty cells respectively as 3 and 2, the results are nearly the same as the results obtained by standard calculations with  $l_{max} = 5$ . Since the number of empty cells is several times more than the number of atomic cells, the efficiency of this calculation is close to the

case where  $l_{pt}$  of all scattering sites is 2. Moreover, the results by Zhang's method are worse than the results of the standard calculations with  $l_{max} = 3$ .

#### 4. conclusion

We have presented an efficient Multiple Scattering formalism based on the partitioning of the scattering matrix  $I - tg$  by a particular orbital angular momentum  $l_{pt}$ . By introducing approximations to the submatrices of  $I - tg$ , the computation of the matrix inversion of  $I - tg$  and Green's function are simplified a lot with a very little loss of accuracy. We have discussed the detailed behaviour of our method for different types of calculations where only parts of the matrix elements of  $\tau$  are needed. We have applied our method to calculate the local DOS of the central atomic sphere of fcc a Cu crystal and a silicon one, and the XAS of graphene. We have found that with small  $l_{pt}$ , the results with our method are nearly the same as the results of the standard calculations with large  $l_{max}$ . With the same values of  $l_{max}$  and  $l_{pt}$ , the accuracy of our method is much higher than that of Zhang's method where more approximations are introduced. Moreover, we have found that in the studies of graphene and silicon, the results of Zhang's method are not satisfactory. A possible reason is that the MT approximation breaks down and the phase shifts of high angular momenta are not negligible anymore.

#### Appendix

In Sec. 2.1, we have introduced basis functions  $\Phi_L$  and it can be expanded as  $\Phi_L(\vec{r}) = \sum_{L'} R_{L'L}(r) Y_{L'}(\hat{r})$ , where  $Y_{L'}(\hat{r})$  are real spherical harmonics. With the radial wavefunction  $R_{L'L}(r)$ , we can compute

$$E_{LL'} = (R_b)^2 W[-i\kappa h_l^+, R_{LL'}] \quad (\text{A.1})$$

and

$$S_{LL'} = (R_b)^2 W[j_l, R_{LL'}], \quad (\text{A.2})$$

where  $R_b$  is the radius of the bounding sphere of the scattering cell.  $j_l$  and  $h_l^+$  denote spherical Bessel and Hankel functions of order  $l$ , respectively. The Wronskians  $W[f, g] = fg' - gf'$  are calculated at  $R_b$ .  $\kappa$  is the electronic momentum relative to the constant interstitial potential.

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